PATENT
TH2306 02 (US)

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the application of	)	
	)	
PAUL M. MCALLISTER ET AL.	)	
	)	
Serial No. 10/815,276	)	Group Art Unit: 1764
	)	
Filed April 1, 2004	)	Examiner: Boyer, Randy
	)	
REACTOR SYSTEM AND PROCESS FOR THE MANUFACTURE OF ETHYLENE OXIDE	)	
	)	

MAIL STOP Amendments
COMMISSIONER FOR PATENTS
P. O. Box 1450
Alexandria, VA 22313-1450

Sir:

DECLARATION UNDER 37 C.F.R. 1.132

The undersigned, Dr. Paul M. McAllister, citizen of the United States of America and residing in Houston, TX, declare and say that:

1. I am a 1987 graduate of the University of Kansas with a Bachelor of Science degree in Chemical Engineering; a 1989 graduate of Notre Dame University with a Master of Sciences degree in Chemical Engineering; and a 1991 graduate of Notre Dame University with a Doctor of Philosophy Degree in Chemical Engineering.

2. In 1991, I joined Shell Oil Company as an Associate Research Engineer in the Environmental Research and Development Department at Shell's Westhollow Research Center. I was involved in the modeling of transport phenomena in porous media and remediation of soil and groundwater.

3. In 1998, I was transferred to the Ethylene Oxide ("EO") Catalyst Department. My activities for Shell have involved technical support for EO producers, modeling of EO catalyst performance, scale up of novel catalysts and carriers from EO catalyst pilot plant to EO catalyst commercial unit, and oversight of the EO catalyst testing facilities.

4. I am currently an inventor on 1 issued U.S. Patent and eleven pending patent applications relating to ethylene oxide processes.

5. I have read the above-identified patent application, the PTO Office Action dated 08/09/07 and the prior art cited by the Examiner (Saito US 4511671; Murphy US 4358623; and Tamura US 4645754).

6. The inventive reactor system provides for an improved balance of the tube packing density, also the bed voidage and the catalyst hold-up, relative to the pressure drop across the packed bed when in use in, for example, ethylene oxide manufacturing, as compared to conventional systems. Figure 1 (see below) shows this unexpected improvement. The data in Figure 1 are plotted as the "test result" versus the inside diameter to outside diameter ("ID/OD") for the various geometries tested. ID/OD is used for simplicity reasons since for a solid cylinder the OD/ID would result in an undefined value making it difficult to plot in a graph.

The "test result" is defined by the quotient of a numerical value of the pressure drop per unit length of the packed bed and a numerical value of the packing density, which numerical values are obtained by testing the packed bed in a turbulent flow of nitrogen gas at a pressure of 1.136 MPa, relative to a comparison quotient of numerical values obtained in an identical manner, except that the hollow cylinder geometric configuration of the same support material is defined by a nominal outside diameter of 8 mm and a nominal inside diameter of 3.2 mm. A decrease in the quotient relative to the comparison quotient is considered a "positive test result" and signifies an improved balance of the tube packing density relative to the pressure drop across the packed bed.

The tube packing density and the pressure drop measurements for the nominal 9, 10 and 11 mm OD supports of Example III of the application text are plotted in Figure 1 in terms of "test result". The ID/OD was calculated using the actual inside and outside diameters of the support. The nominal 9 mm OD supports had actual average outside diameters ranging from 9.1 to 9.3 mm. The nominal 10 mm OD supports had actual average outside diameters ranging from 10.4 to 10.7 mm. The nominal 11 mm OD supports had actual average outside diameters ranging from 11.5 to 11.6 mm. Nominal 8 mm outside diameter support cylinders having actual average bore sizes of 3.27, 2.90, 2.70, 1.96, 1.30, and 0.78 mm along with a support with no hole (internal diameter defined as 0 mm) were tested against a nominal 8 mm OD support cylinder having a standard actual average bore size of 3.2 mm. The nominal 8 mm OD supports had actual average outside diameters ranging from 8.4 mm to 8.7 mm. The tube packing density and pressure drops were measured according to Example III of the application text.

As can be observed from Figure 1, the "test result" increases for ID/OD values approaching 0 and greater than 0.37 (i.e., OD/ID of less than 2.7). Such increases in the "test result" indicate a less desirable geometry (i.e., the pressure drop penalty is more significant than the packing density benefit or the tube packing density penalty is more significant than the pressure drop benefit). This is truly

unexpected especially in light of what would have been predicted for pressure drop by a commonly accepted scientific correlation (the Ergun Correlation).

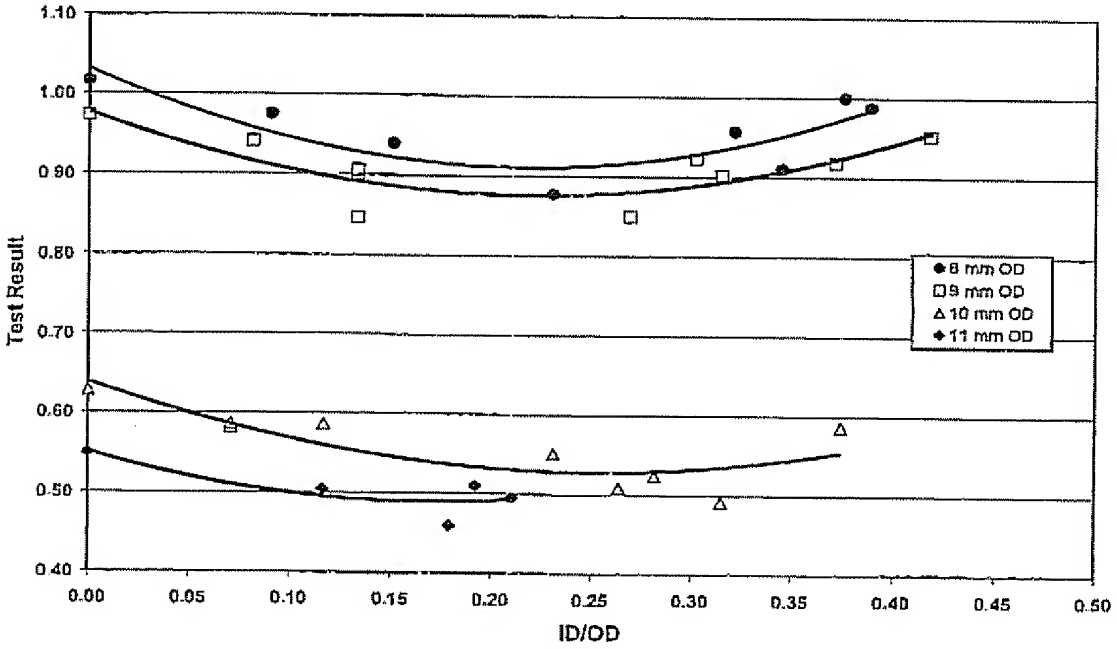

Figure 1

This Ergun Correlation is shown below:

$$\frac{\Delta P}{L} = C_1 \frac{\mu V_o}{D_p^{\,2}} \frac{(1-\varepsilon)^2}{\varepsilon^3} + C_2 \frac{\rho V_o^2}{D_p} \frac{(1-\varepsilon)}{\varepsilon^3} \qquad \text{(EC)}$$

Where,

$\frac{\Delta P}{L}$ is the pressure drop per unit reactor length,

V_o is the superficial gas velocity,

μ is the gas viscosity,

ε is the void fraction of the packed bed external to the supports,

ρ is the gas density,

D_p is the effective particle diameter,

C_1 is the laminar term coefficient,

and

C_2 is the turbulent term coefficient.

The effective particle diameter can be defined as:

$$D_p = 6\frac{V_{solid}}{A_{exterior}} \qquad (D_p)$$

Where,

V_{solid} is the geometric solid volume of each particle,

and

$A_{exterior}$ is the geometric external surface area of a particle.

For the high Re_{tube} conditions used in this testing and typical for EO reactors, the first term of Equation (EC), which is proportional to the velocity, is small relative to the second term, which is proportional to the velocity squared. Thus, it was found that the first term could be neglected, and the measured pressure drops were proportional to the product of the average gas density and the average superficial velocity squared. This turned out to be true for all conditions and carrier samples tested.

8. The nominal 8 mm outside diameter ("OD") support cylinder having actual average bore sizes of 3.27, 2.90, 2.70, 1.96, 1.30, and 0.78 mm along with a support with no hole (internal diameter defined as 0 mm) were tested against a nominal 8 mm OD support cylinder having a standard actual average bore size of 3.2 mm. After each support sample was loaded in the test vessel, the pressure drop and tube packing density was measured according to Example III of the application text.

All the parameters in the Ergun Correlation (EC) can be calculated from the hollow cylinder characterization information. The value of C_2 was specified as 1.75 (R. B. Bird, W.E. Stewart, and E.N. Lightfoot, p. 200, Transport Phenomena, John Wiley & Sons (1960)). The tube packing density was measured for the nominal 8 mm OD supports. Figure 2 below shows the expected "test result" based on the predicted pressure drop as calculated by the Ergun Correlation and the measured tube packing density for the various bore sizes of the 8 mm OD cylinders. Figure 2 also shows the measured "test result" values for the same 8 mm OD supports. Using the Ergun Correlation, one would expect significant increases in pressure drop and the "test result" as the ID decreases from 3.2 mm to 0 mm with nominal 8 mm OD cylinders. As shown in Figure 2, the "Test Result" values calculated using the Ergun pressure drop equation did not agree well with the Experimental "Test Result" values. Much higher pressure drop values were predicted by the Ergun Correlation with reduced ID and the test result increased monotonically as the ID/OD ratio was decreased. In contrast, the experimental results demonstrated a minimum in the value of the Test Result. This demonstrates an unexpected benefit in the balance of pressure drop and packing density with reduced ID cylinders.

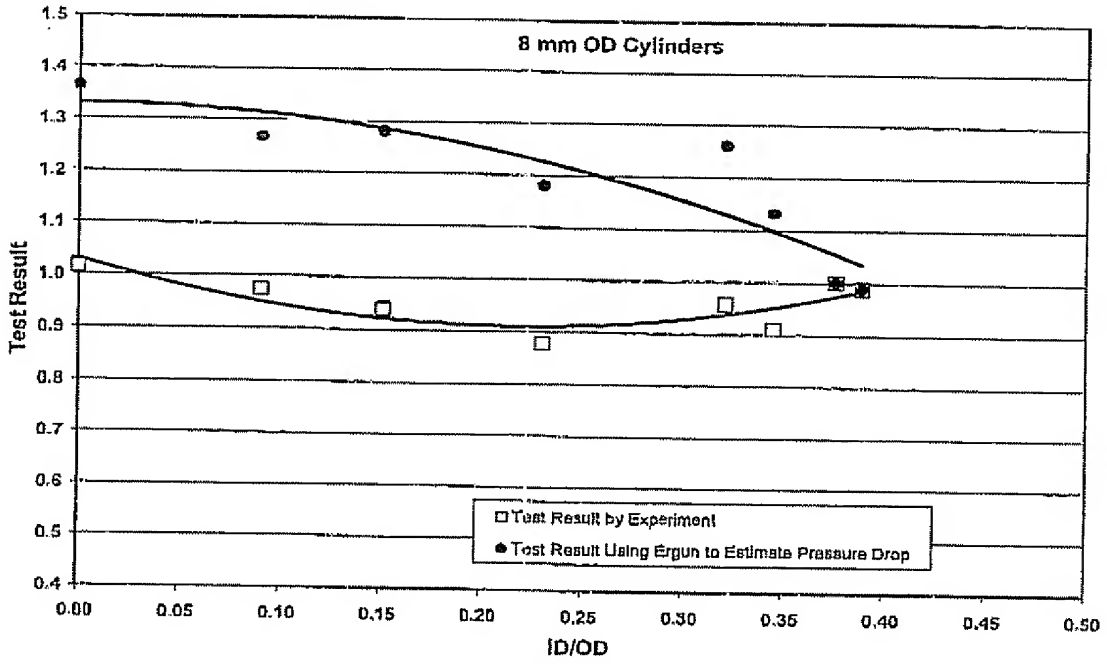

Figure 2

As discussed above, it was truly **unexpected** that the combination of a large tube diameter (at least 28 mm) and a hollow cylinder geometry for nominal 8, 9, 10, and 11 mm supports having a small inside diameter, according to the present invention, would result in an improved balance of tube packing density relative to the pressure drop across the packed bed. In particular, it is unexpected that the tube packing density is improved relative to the standard 8 mm OD support without the expected increase in pressure drop across the packed bed.

9. While the size and shape of the support for EO catalysts and the reactor tube diameter are variable factors, prior to the subject patent application, it would have been predicted by the Ergun Correlation that support shapes with such small internal diameters would not be acceptable for commercial EO production (i.e., the pressure drop would be too high). Therefore, the invention claimed in the subject patent application is unexpected, and would not be expected by any reasonable reading of the Saito et al., Murphy et al., and Tamura et al. cited art.

10. Saito et al. relates to a catalyst for producing methacrolein. Saito et al. discloses a catalyst having a certain general formula molded into the shape of a hollow cylinder having an outside diameter from 3.0 to 10.0 mm, an inside diameter from 0.1 to 0.7 times the outside diameter, and a length from 0.5 to 2.0 times the outside diameter. Saito et al. teaches that the disclosed catalyst has improved selectivity and yield compared to spherical or solid cylinder shapes. The key to the improvement in catalyst performance is attributed to the increase in the geometric surface area of the catalyst compared to a solid cylinder. The increase in geometric surface area allows the methacrolein product to diffuse more rapidly than with a solid cylinder reducing the consecutive reaction of

methacrolein to methacrylic acid, acetic acid, carbon dioxide, and carbon monoxide. *See U.S. Patent No. 4,511,671*, col. 1, ll. 35-44; col 1, l. 51 – col. 2, l. 20; col. 2, ll. 25-33. Thus, the methacrolein reaction of Saito et al. is a diffusion-limited reaction with an effectiveness factor significantly less than 1.

Intrapellet diffusion is correlated by an effectiveness factor (i.e., actual reaction rate/reaction rate without the influence of pore diffusion). The maximum value for the effectiveness factor is 1. The ethylene epoxidation system is not a diffusion-limited reaction; therefore, it has an effectiveness factor of essentially 1 for the supports included in the subject patent application. In a diffusion-limited reaction system, as the diameter of a pellet is reduced, the effectiveness factor increases. Additionally, for a hollow cylinder, the effectiveness factor also increases as the inside diameter is increased relative to the outside diameter. These trends are observed in the working examples of Saito et al., reinforcing that it is a diffusion-limited reaction.

In the working examples of Saito et al., methacrolein was produced using a reaction tube having a diameter of 25.4 mm and containing catalyst having a nominal outside diameter ranging from 4 to 8 mm. *Id.* at col. 4, ll. 21-22; Table 1. Examples 1-3, 9 and Comparative Examples 1-2 all used the same catalyst formulation and test conditions but varied the shapes of the hollow cylinders. The conversion of isobutylene; the selectivity to methacrolein, the one-pass yield of methacrolein, the temperature difference between the reaction temperature and the temperature of a hot spot, and the pressure drop across the catalyst bed was among the data provided in Tables 1 and 3 of Saito et al. As can be observed from the data for the nominal 6 mm catalysts, increasing the geometric surface area of the support (by increasing the inside diameter) provided improved catalyst performance resulting from the increase in the effectiveness factor. The best set of performance data out of these examples was for the 6 mm OD, 3 mm ID, 6.6 mm length catalyst that had the highest surface area. Further, the next best set of data out of these examples was for the 5 mm OD, 2 mm ID, 5.5 mm length catalyst. This is attributable to the reduced outside diameter of the catalyst, which also increases the effectiveness factor resulting in improved catalyst performance.

The examples further demonstrate that the methacrolein process of Saito et al. is a diffusion-limited reaction since an increase in yield and conversion was observed with reduced packing density (i.e., less catalyst in the reaction tube) when operated at a constant temperature. This is opposite from the ethylene epoxidation process, where reduced packing density leads to lower conversion and yield.

Figure 3 below demonstrates how differently the behavior of Saito et al.'s system is compared to the ethylene epoxidation system. The relative yield (methacrolein or ethylene oxide) is plotted versus the relative density for the 6 mm OD cylinder data of Examples 1-3 and Comparative Examples 1-2 of Saito et al. and for a high selectivity catalyst for ethylene epoxidation. For the ethylene epoxidation case, a base case tube packing density of 908 kg/m^3 was defined. Then, the tube packing density was varied in a predictive model from 650 to 1100 kg/m^3. The relative density for each case was taken as the ratio of the tube packing density divided by 908 kg/m^3. In the Saito case, the

geometric volume of each hollow cylinder was divided by the geometric volume of the solid 6 mm OD support to determine the relative density. The relative density for the 6 mm OD cylinders was calculated from the data provided in Table 1 of Saito et al. The ethylene epoxidation data for several different relative density values was obtained using a predictive model assuming constant feed flow, composition and coolant temperature (as indicated in Saito et al.'s examples). The predictive model was based on the correlation of actual catalyst performance data gathered from numerous sources such as micro-reactor data, pilot plant data, and commercial plant data. The model was for a high selectivity catalyst comprising silver, rhenium and tungsten, as described in U.S. 4,766,105.

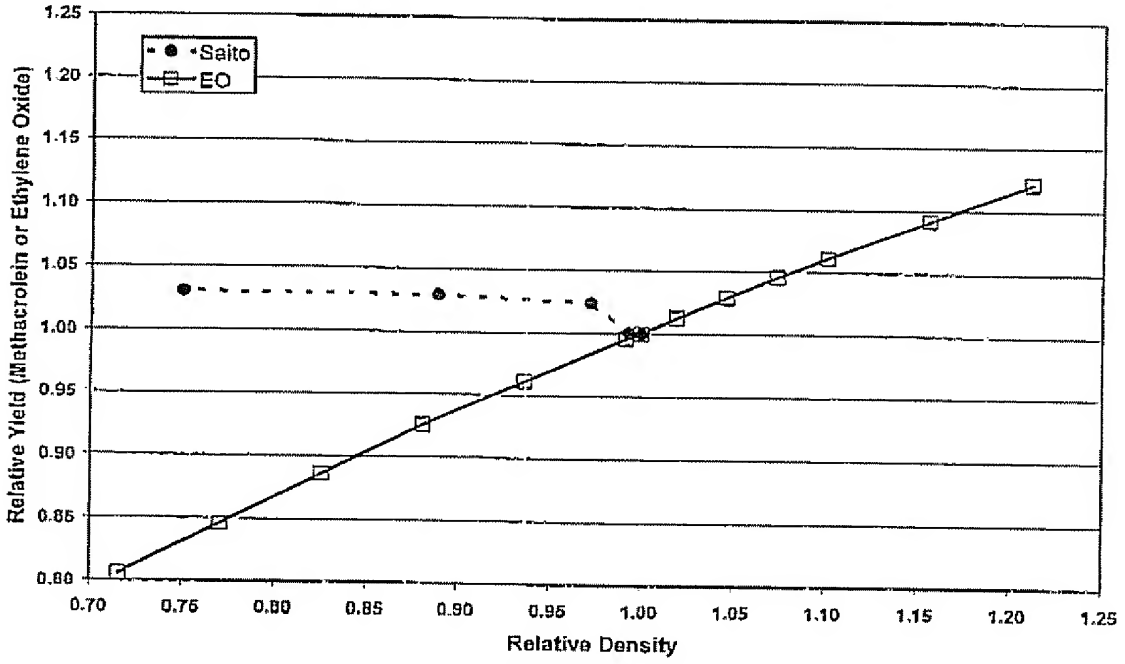

Figure 3

Based on the results from Saito et al., the yield of desired product increases with lower mass of catalyst in the reactor. However, for the ethylene epoxidation system, the yield clearly benefits from the greater catalyst mass. This demonstrates that Saito et al. is a diffusion-limited reaction whereas the ethylene epoxidation reaction is not. Thus, there are different considerations that will be taken into account for each of the different reactions. In particular, for the diffusion-limited system in Saito et al., one skilled in the art would want to increase the effectiveness factor by reducing the pellet size and/or increasing the inside diameter to decrease the mass of catalyst in the reactor unlike for the present invention where the inside diameter is decreased for large OD supports of 8, 9, 10, and 11 mm in order to improve the tube packing density (i.e., greater mass in the reactor) which also unexpectedly improves the balance of tube packing density relative to the pressure drop across the packed bed.

11. The Examiner asserts that Saito et al. uses a 25.4 mm reaction tube in his examples and contemplates use of his system for industrial production which implies a scale-up of his system to a larger size since his invention is in no way limited to tube size as long as the other parameters of his invention are satisfied. However, the tube diameter of 25.4 mm, used in the examples of Saito et al., is of an industrial scale; therefore, the skilled person would scale-up his system by multiplication (i.e., use a multitubular reactor with many tubes having a diameter of 25.4 mm). This is the logical scale-up scenario since an object of Saito et al. is to eliminate hot spots in the catalyst layer in the reactor. The working examples of Saito et al. specifically measure the temperature difference between the reaction temperature and the temperature of the hot spot. *See US 4,511,671*, col. 1, ll. 21-29; ll. 35-38; col. 4, ll. 27-31. Thus, a key consideration of Saito et al. is heat transfer out of the packed bed. It is generally known that the area for heat transfer per unit volume decreases as the tube diameter increases. Therefore, the skilled person would not have a reason to modify Saito et al. to use tube diameters larger than 25.4 mm.

Based on the additional evidence submitted above, the invention claimed in the instant patent application would not be obvious by any reasonable reading of Saito et al.

12. Murphy et al. relates to post-conversion cooling of formaldehyde-containing gases in an array of externally cooled tubes containing inert balls which are relatively large in comparison with the inside diameter of the tubes. The Examiner points to column 3, lines 50 to 53 of Murphy et al. for support that packing density is a result-effective variable and changes in packing density will necessarily result in corresponding changes in pressure drop per unit length of a packed bed. The disclosure in Murphy et al. states that small solid bodies such as beads can result in an increase in pressure drop. Murphy et al. also discloses at column 4, lines 32-35 that the pressure drop across a packed bed of the relatively large balls of his invention is significantly less than the pressure drop across a packed bed of beads. This disclosure is in agreement with the Ergun Correlation, which would predict an increase in pressure drop per unit length for beads (i.e., balls of a very small size) compared to larger balls.

As discussed above, it has been found that the combination of a large tube diameter (at least 28 mm) and a hollow cylinder geometry for nominal 8, 9, 10, and 11 mm supports having a small inside diameter, in accordance with the present invention, **unexpectedly** results in an improved balance of tube packing density relative to the pressure drop across the packed bed. In particular, it is unexpected that the tube packing density is improved relative to the standard 8 mm OD support without the expected increase in pressure drop across the packed bed.

Based on the additional evidence submitted above, the invention claimed in the instant patent application would not be obvious by any reasonable reading of Saito et al. in combination with Murphy et al.

13. Tamura et al. relates to a silver catalyst for production of ethylene oxide wherein the catalyst comprises a support in the form of Intalox saddles or Berl saddles. Tamura et al. teaches that the carrier shape is selected such that during the epoxidation process

stagnation of the gas in the catalyst particles is avoided, in particular it is desired that the ratio of the apparent surface area of the catalyst to the apparent volume is large. The Intalox saddles or Berl saddles have the desired large ratio of apparent surface area to apparent volume. Tamura et al. also discloses that for Raschig rings in order to increase the ratio of apparent surface area to apparent volume the inside diameter is increased (which decreases the wall thickness). *See U.S. Patent No. 4,645,754*, col. 3, l. 66 – col. 4, l. 18. This teaches away from the present invention.

Further, Tamura et al. teaches that the Intalox saddles or Berl saddles have a lower packing specific gravity for a fixed grain size and wall thickness than Rachig rings and such saddles suffer only a minimal pressure loss across the catalyst bed. *Id.* at col. 4, ll. 25-51. This also teaches away from the present invention where it has been found that the combination of a large tube diameter (at least 28 mm) and a hollow cylinder geometry for nominal 8, 9, 10, and 11 mm supports having a small inside diameter, in accordance with the present invention, **unexpectedly** results in an improved balance of tube packing density relative to the pressure drop across the packed bed.

The Examiner asserts that "while Saito notes that the hollow cylindrical catalyst support structures naturally result in lower pressure drops across reactor beds using such structures (i.e., lower than would be possible with support structures having other shapes) . . . , the *porous* catalytic support structures of Tamura would be expected to result in an even lower pressure drop than achievable by using the structures of Saito." *See Office Action mailed August 9, 2007*, paragraph bridging pages 10 and 11. First, the lower pressure drop naturally resulting from the hollow cylinder shape of Saito et al. is compared to a solid cylinder and not other shapes in general. Second, the porous catalytic support material of Tamura et al. would not be expected to result in an even lower pressure drop. The porosity of the support material used to form the shaped supports, as described in Tamura et al., has a negligible effect on pressure drop of a packed bed. Tamura et al. teaches that the use of Intalox saddles or Berl saddles instead of spheres or Raschig rings results in a catalyst having high selectivity while experiencing only minimal pressure loss in the catalyst bed. *U.S. Patent No. 4,645,754*, col. 3, ll. 29-40. Further, combining the Intalox saddles or Berl saddles of Tamura et al. with the system of Saito does not bring the skilled person closer to the present invention.

Based on the additional evidence submitted above, the invention claimed in the instant patent application would not be obvious by any reasonable reading of Saito et al. in combination with Tamura et al. or Saito et al. in combination with Tamura et al. and Murphy et al.

14. I declare further that all statements made herein of my knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Respectfully submitted,

Paul M. McAllister

This 7 day of February, 2008